

THE KINETICS OF CATALYTIC HYDROGENATION OF
POLYNUCLEAR AROMATIC COMPONENTS IN
COAL LIQUEFACTION SOLVENTS*

H. P. Stephens and R. J. Kottenstette

INTRODUCTION

Although the importance of polynuclear aromatic hydrocarbons (PAHs) as hydrogen transfer agents in coal liquefaction has been well established (1,2), there have been few studies of the kinetics of the formation of hydroaromatic donor forms by catalytic hydrogenation. This paper presents the results of hydrogenation experiments performed with single component PAH solutions in an inert solvent and with a complex, multicomponent coal-derived liquid. The rate of hydrogenation of one PAH component found in coal-derived liquids, pyrene, was followed and used to illustrate the impact of reaction conditions on the kinetics and thermodynamics of catalytic hydrogenation of PAHs in liquefaction solvents. The results show that the catalytic hydrogenation behavior of PAHs in complex coal-derived liquids is analogous to that of a single component system. In addition, this study clearly demonstrates PAHs in coal-derived liquids can be quantitatively hydrogenated to donor-solvent products at temperatures as low as 100°C.

EXPERIMENTAL

To establish the thermodynamic behavior of the hydrogenation of pyrene to 4,5-dihdropyrene, reactions were performed over a wide range of conditions: temperatures from 275 to 400°C and pressures from 500 to 2000 psig. Subsequent kinetic experiments with pyrene and the coal-derived liquefaction solvent were performed at 100 and 300°C and hydrogen pressures of 100 and 500 psig.

Materials

Pyrene and n-hexadecane, an inert solvent for the pyrene experiments, were used as received from Aldrich Chemical Company. The coal-derived liquid studied was a hydrogenated Koppers creosote oil used as a start-up solvent in pilot two-stage coal liquefaction experiments (3). Prior to use, it was catalytically dehydrogenated under nitrogen at 425°C. This converted all but approximately 10% of the hydropyrenes to pyrene. Two catalysts were employed for these experiments. Shell 324 M, a Ni-Mo/Alumina catalyst currently used in the second stage of integrated two-stage pilot plant operations (4), was added in its presulfided form to experiments at 275°C and above. Because Shell 324 has a low activity at temperatures below 250°C, reactions performed at 100°C were

* This work supported by the U. S. Department of Energy at Sandia National Laboratories under contract DE-AC04-76DP00789.

catalyzed with a novel catalyst under development, palladium hydrous titanate (5,6). Both catalysts were added to the reactors as -200 mesh powders. High purity hydrogen was used in all experiments.

Apparatus and Procedure

Batch reactions were performed in stainless steel microreactors (7), equipped with thermocouples and pressure transducers. Four reactors could be operated simultaneously. After the reactors were charged with the reactants and catalyst, they were pressurized with hydrogen and heated to temperature (heat-up time \approx 1 min) in a fluidized sand bath while being horizontally shaken at 160 cycles/min. Temperatures and pressures were recorded with a digital data acquisition system during the course of the experiments. Following the heating period, the reactor vessels were quenched (time of quench \approx 10 sec), and the products were removed for analysis.

A separate set of experiments was used to establish that catalyst particle size and reactor agitation rate were sufficient to prevent reaction rate retardation due to mass transfer limitations. It was estimated from reactor heat-up and quench rates that time at temperature could be determined to within 0.5 min. Temperatures and pressures were maintained at the nominal values to within $\pm 2^\circ\text{C}$ and ± 20 psig respectively.

Product Analyses

The products were washed from the reactor with toluene, filtered to remove catalyst and transferred to a volumetric flask. Following the addition of internal standards, 2-methylnaphthalene for the hydrogenation of pyrene in n-hexadecane and n-tridecane for the creosote oil experiments, the product solutions were brought to a known volume and analyzed by gas chromatography.

Packed column chromatography [Hewlett-Packard 5840A with flame ionization detection (FID)] was sufficient for analysis of the products from the pyrene reactions. Column and chromatographic conditions were: 1/8 in x 10 ft. column with Supelco 10% Sp-2100 on 100/120 Supelcoport, 220°C , $20\text{ cm}^3/\text{min}$ nitrogen carrier gas. However, separation of the product components of the creosote oil experiments required high-resolution chromatography (Hewlett Packard 5880A with FID) and a capillary column: 0.2 mm ID x 30 m long SE 54; $0.56\text{ cm}^3/\text{min}$ helium carrier flow; 100:1 split ratio injection; and a temperature ramp from 120 to 270°C at $2^\circ\text{C}/\text{min}$.

Gas chromatography/mass spectrometry techniques were used to identify the order of elution of pyrene and hydrogenated products. An external standard consisting of a solution of the internal standard, pyrene, n-hexadecane and 1,2,3,6,7,8-hexahdropyrene was used to establish FID response factors relative to the internal standards. The weights (W) of each

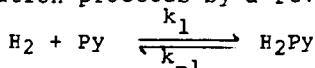
component of the product mixture were calculated from the chromatograph area (A), the response of the standard (R_S) and the relative response factor (R_R):

$$W = R_R \cdot R_S \cdot A$$

RESULTS AND DISCUSSION

Thermodynamic Behavior

Qualitative aspects of the hydrogenation of pyrene in n-hexadecane at the higher temperatures of this study can be observed in Figure 1, a plot of the ratio of 4,5-dihydropyrene (H_2Py) to pyrene (Py) concentration as a function of time for experiments performed at 300°C and 500 psig. As can be seen, $[H_2Py]/[Py]$ approaches a constant value which indicates that hydrogenation proceeds by a reversible reaction:



Thus, the maximum (equilibrium) concentration of dihydropyrene $[H_2Py]_e$ which can be formed is limited by the hydrogen pressure P and the value of the equilibrium constant K_p for the reaction:

$$[H_2Py]_e = P K_p [Py]_e$$

Results of the experiments at 300°C and 500 psig with creosote oil, Figure 2, have established that the dihydropyrene to pyrene ratio exhibits a similar, though much slower, approach to an equilibrium value.

Results of more than 50 catalytic hydrogenation experiments with pyrene over a wide range of temperatures (275 to 400°C), hydrogen pressures (500 to 2000 psig) and reaction times (5 to 120 minutes) have established the temperature dependence of K_p , as calculated from the pressures and equilibrium concentration ratios of $[H_2Py]_e$ to $[Py]_e$:

$$K_p = \frac{1}{P} \frac{[H_2Py]_e}{[Py]_e}$$

A van't Hoff plot of these values is given in Figure 3. Linear regression of the data yields the temperature (degrees Kelvin) dependence of K_p for the hydrogenation of pyrene to dihydropyrene:

$$\ln K_p = \frac{5330}{T} - 15.86$$

Extrapolation of this equation shows that low temperature hydrogenation greatly favors the formation of dihydropyrene. For example, consider hydrogenation at 500 psig and two temperatures 400°C and 100°C. Although conversion of pyrene to dihydropyrene is limited to 15% at 400°C, equilibrium

conversion at 100°C is greater than 99%. Thus, at high temperatures pyrene hydrogenation is a reversible process, while at low temperatures, it is essentially an irreversible process. In addition, higher values of K_p at low temperatures permit a substantial reduction in hydrogen pressure to achieve comparable or better conversions.

Kinetics

For reversible reactions, the approach to equilibrium can be modeled as a first-order process with an effective rate constant equal to the sum of the forward and reverse rate constants (8):

$$\ln \frac{X_e}{X_e - X_t} = (k_1 + k_{-1})t$$

where X_t and X_e are the extents of reaction at time t and at equilibrium. For pyrene

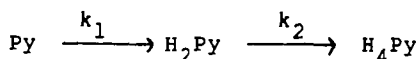
$$X_t = \frac{[H_2Py]_t}{[Py]_t + [H_2Py]_t}$$

and

$$X_e = \frac{P K_p}{1 + P K_p}$$

Figure 4 shows a plot of $\ln (X_e/(X_e - X_t))$ vs time at 300°C and 500 psig for the hydrogenation of pyrene in n-hexadecane and Figure 5 shows a similar plot for the hydrogenation of pyrene in creosote oil. As can be seen, although the rate of hydrogenation of pyrene in the complex solvent may be modeled by pseudo first-order reversible kinetics, the rate constant on a catalyst weight basis is two orders of magnitude smaller. This can be attributed to the presence of many other species in the creosote oil which compete with pyrene for active sites on the catalyst.

That catalytic hydrogenation of pyrene proceeds by an essentially irreversible reaction path at low temperatures is demonstrated by the results of experiments with pyrene in n-hexadecane catalyzed with palladium hydrous titanate at 100°C and 100 psig. Two major products, 4,5-dihydropyrene (H_2Py) and 4,5,9,10-tetrahydropyrene (H_4Py) are formed under these conditions. Initial experimentation showed that although the concentration of H_4Py increased monotonically with reaction time, the concentration of H_2Py reached a maximum, then decreased. Because this behavior indicates an irreversible series reaction path,



the results of additional experiments (% conversion to H₂Py vs % conversion to H₄Py) were plotted on a series reaction diagram, Figure 6. An excellent fit of the data to a hyperbolic series reaction path expression was obtained:

$$Y + S(X-100) = S(Y+X-100)^{1/S}, \quad S \neq 1$$

where Y = % conversion to H₂Py
 X = % conversion to H₄Py
 S = selectivity = $k_1/k_2 = 1.5$

Therefore, the rate of disappearance of pyrene can be modeled, as shown by Figure 7, by irreversible first-order kinetics:

$$\ln \frac{[Py]_t}{[Py]_0} = k_1 t$$

where $[Py]_0$ is the initial concentration of pyrene.

That pyrene in a complex liquefaction solvent can be hydrogenated irreversibly at low temperatures was demonstrated by hydrogenation of creosote oil at 100°C and 500 psig for 30 minutes with palladium hydrous titanate catalyst. No pyrene could be detected in the hydrogenated creosote oil following the reaction. It was completely converted to hydrogenated products.

CONCLUSION

The ultimate application of this study is to provide guidance for establishing optimum conditions for hydrogenation of coal liquefaction process solvents. The results presented here show that high temperature catalytic hydrogenation of PAH hydrogen donor precursors such as pyrene is reversible and that the maximum conversion to dihydropyrene is thermodynamically limited by a low value for the equilibrium constant K_p . Because a higher value of K_p at low temperatures favors formation of the hydroaromatic product, conversion at low temperatures is kinetically limited. However, advantages of low temperature hydrogenation include quantitative conversion of PAHs to hydroaromatics and a substantial reduction of the hydrogen pressure. Additionally, this study has clearly demonstrated that satisfactory hydrogenation rates at low temperatures may be achieved by using more active catalysts, such as palladium hydrous titanate.

REFERENCES

1. D. D. Whitehurst, T. O. Mitchell and M. Farcasiu, Coal Liquefaction, Academic Press, New York (1980).
2. E. Gorin, "Fundamentals of Coal Liquefaction," p. 1845-1918, in Chemistry of Coal Utilization, 2nd Supplementary Volume, Martin A. Elliot, Ed., Wiley-Interscience, New York (1981).
3. H. D. Schindler, J. M. Chen, M. Peluso and J. D. Potts, "Liquefaction of Eastern Bituminous Coals by the ITSL Process," Proceedings of the 7th Annual EPRI Contractors Conference on Coal Liquefaction, Palo Alto, CA, May 12, 1982, Electric Power Research Institute (1982).
4. M. J. Moniz, R. S. Pillai, J. M. Lee and C. W. Lamb, "Process Studies of Integrated Two-Stage Liquefaction at Wilsonville," Proceedings of the 9th Annual EPRI Contractors' Conference on Coal Liquefaction, May 8-10, 1984, Palo Alto, CA, Electric Power Research Institute.
5. H. P. Stephens, R. G. Dosch and F. V. Stohl, Preprints of Papers, American Chemical Society, Fuel Division, Vol. 28, No. 1, p. 148 (1983).
6. H. P. Stephens, R. G. Dosch and F. V. Stohl, Ind. Engr. Chem., Prod. R&D, in press (1985).
7. R. J. Kottenstette, SAND-82-2495, Sandia National Laboratories, Albuquerque, NM, March 1983.
8. J. W. Moore and R. G. Pearson, Kinetics and Mechanisms, 3rd Ed., John Wiley & Sons, New York (1981).

FIGURE 1. $[H_2 Py]/[Py]$ vs. time for hydrogenation of pyrene (100 mg) in n-hexadecane (1.0 g), 300 C, 500 psig, 15 mg 324M

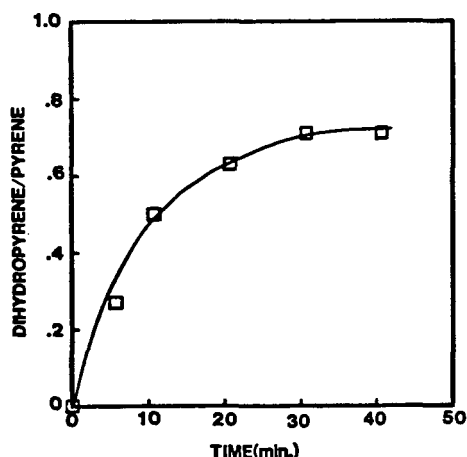


FIGURE 2. $[H_2Py]/[Py]$ vs. time for hydrogenation of dehydrogenated creosote oil (1.0 g), 300 C, 500 psig, 100 mg 324M

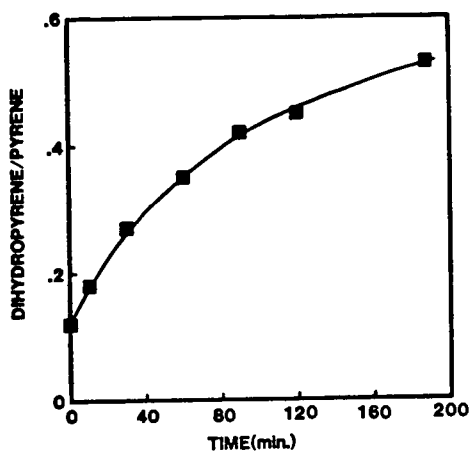


FIGURE 3. van't Hoff plot for hydrogenation of pyrene to dihydropyrene, 275 to 400 C

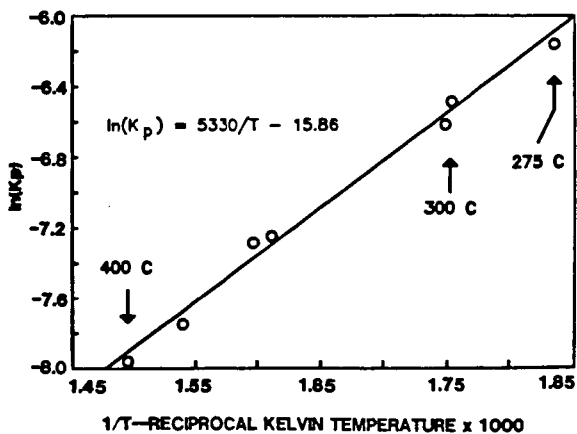


FIGURE 4. Pseudo first-order reversible kinetic plot for hydrogenation of pyrene in n-hexadecane

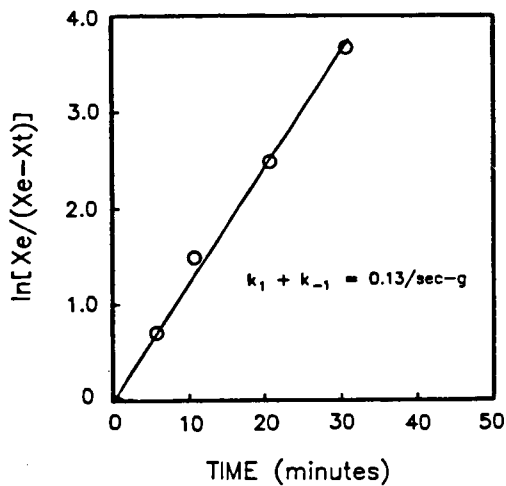


FIGURE 5. Pseudo first-order reversible kinetic plot for hydrogenation of pyrene in dehydrogenated creosote oil

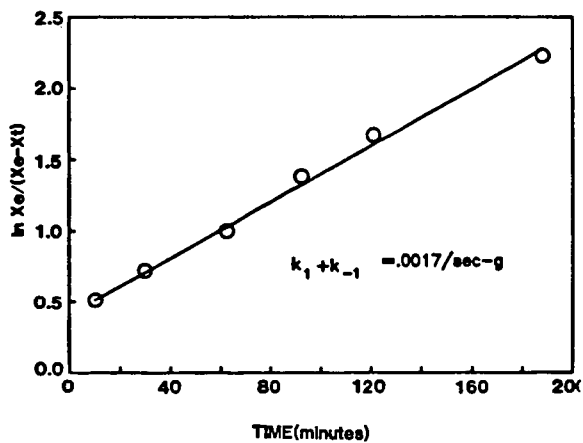


FIGURE 6. Series reaction diagram for hydrogenation of pyrene to di- and tetrahydopyrenes, 100 C, 100 psig

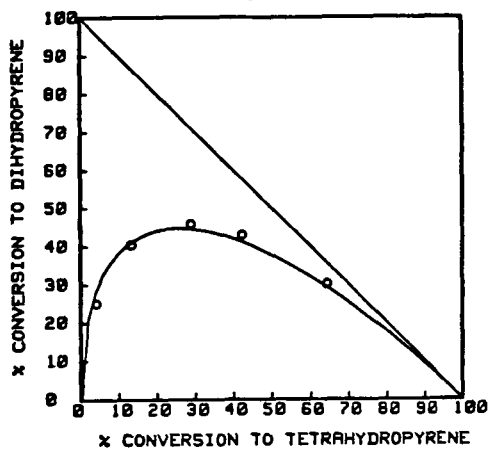


FIGURE 7. Irreversible kinetic plot for hydrogenation of pyrene (100 mg) in *n*-hexadecane (1g), 100 C, 100 psig, 18 mg Pd titanate

